Phase stability, chemical bonds, and gap bowing of In$_x$Ga$_{1-x}$N alloys: Comparison between cubic and wurtzite structures

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Thermodynamic, structural, and electronic properties of wurtzite In$_x$Ga$_{1-x}$N alloys are studied by combining first-principles total energy calculations with the generalized quasichemical approach, and compared to previous results for the zinc-blende structure. Results for bond-lengths, second-nearest-neighbors distances, and bowing parameter are presented. We observed that the wurtzite results are not significantly different from the ones obtained previously for the zinc-blende structure. The calculated phase diagram of the alloy shows a broad and asymmetric miscibility gap as in the zinc-blende case, with a similar range for the growth temperatures, although with a higher critical temperature. We found a value of 1.44 eV for the gap bowing parameter giving support to the recent smaller band gap bowing findings. We emphasize that other theoretical results may suffer from incomplete sets of atomic configurations to properly describe the alloy properties, and experimental findings. Moreover one must take into account a broad composition range in order to obtain reliable results.

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I. INTRODUCTION

In the past decade remarkable progress has been made in the development of optical and electronic devices based on group-III nitrides AlN, GaN, InN, and their alloys. Light emitting diodes and laser diodes operating in the green-blue-UV spectral region and high-frequency, high-power, and high-temperature electronic devices have been successfully fabricated.[1–7] A common feature of these device structures is the use of ternary In$_x$Ga$_{1-x}$N or Al$_x$Ga$_{1-x}$N alloys. Alloying among the group-III nitrides allows a change in the band gap from 1.89 eV in InN to 6.28 eV in AlN with an intermediate value of 3.44 eV for GaN (at 300 K).[8] However, recent reports state the value of 0.70–0.90 eV for the energy gap of InN, which allows an even wider range of variation for the band gap,[9–14] that can now be tuned from the near infrared to the deep ultraviolet. This wide spectral range offers possibilities for the use of group-III nitrides in a variety of device applications. For instance, the energy gaps available in the InGaN alloy system provide an almost perfect match with the complete solar spectrum, which makes InGaN a potential material for high efficiency multijunction solar cells.[15,16] With this narrowed gap of InN, it becomes necessary to reevaluate many of the material parameters of InN and their composition dependence in group-III-nitride alloys, e.g., the bowing parameter.[15–17]

Under ambient conditions AlN, GaN, and InN crystallize in the hexagonal wurtzite (*W*) structure. Although, epitaxial AlN, GaN, and InGaN layers have also been successfully grown on in the metastable zinc-blende (ZB) phase,[18–20] up to now, quaternary nitride-based alloys were grown only in the *W* structure. In the wurtzite structure the four nearest neighbors of an atom are located at the corners of a slightly deformed tetrahedron that surrounds the central atom symmetrically, which (in the case of the nitrides) is compressed

in the direction of the *c* axis. The degree of deformation depends on the ratio *c*/*a*. If the *c*/*a* ratio has the ideal value of $\sqrt{8/3}=1.633$ and if the single internal coordinate of the structure is equal to 3/8 of the corresponding wurtzite structure, the nearest-neighbor atoms are positioned at exactly the same sites as in a crystal having zinc-blende structure. Despite the close structural similarities between these two phases, their electronic structures are different.[21] The study of the ZB-*W* polytypism stability in the III-V and II-VI semiconductors and the differences in their electronic structure has attracted considerable attention up to now.[21–26]

There are theoretical studies of the properties of the *W*-InGaN alloy and all of them use very simplified models.[17,27–32] To the best of our knowledge, there is no theoretical work reported so far which contemplates, in an equal footing, both, a reasonably sized model supercell and the statistics of the alloy. All of them use only one or very few alloy configurations. While for the wurtzite structure the calculations were more simplified, for the zinc blende one there are a set of rigorous works which comply with alloy statistics.[33–38] The absence of rigorous calculations performed for the *W* structure maybe justified for the following reasons: (a) structural similarities between *W* and ZB structures; (b) there is a common expectation that the ZB and *W* alloys should have approximately the same properties, including, for example, the bowing parameter for the energy gap and critical temperature under which there is alloy phase separation;[6,39] and (c) the calculation procedure is simpler for ZB than for *W* structure, since for the ZB calculations only one lattice constant must be optimized, while for the *W*, it is necessary to optimize the three lattice parameters: the lattice constants *c*, *a*, and the internal parameter *u*, which extremely increases the number of necessary calculations. In the literature one sees arguments in favor and against a ZB calculation as a equivalent to *W*, but proper proofs are not

presented. Therefore, it should be of great use and interest to perform a rigorous study of the alloy properties in both structures by using the same methods, in order to confirm the expected similarities and/or study the differences between the two structures.

In this work, we present a rigorous theoretical study of thermodynamic, structural and electronic properties of ternary $In_xGa_{1-x}N$ bulk nitride alloys in the *wurtzite* structure and compare to previous results of the ZB structure obtained by the same research group by using the same method.[33] The calculations performed here for InGaN are based on an *ab initio* pseudopotential plane-wave method, and a generalization of the quasichemical approach combined with a cluster expansion of the thermodynamic potentials. It has been demonstrated that this model is able to successfully describe the physical properties of group-III nitride alloys.[33–36] Here, we are going to focus in particular on the phase diagram of the W-$In_xGa_{1-x}N$ alloy, its lattice constants and chemical bonds, through first- and second-nearest neighbor distances, and the band gap behavior as a function of the alloy composition x. A comparison with the experimental findings is also made.

The paper is organized as follows. Section II describes the theoretical methods adopted for the calculations, while the results and a detailed discussion of the alloy behavior and properties are given in Sec. III. Finally, Sec. IV is devoted to the conclusions.

II. THEORETICAL MODEL

The generalized quasichemical approximation (GQCA) and the cluster expansion method are described elsewhere.[33,40,41] Therefore, we will mention them only briefly. The alloy is described as an ensemble of clusters individually independent statistically and energetically of the surrounding atomic configuration. Each cluster j with a certain number of In and Ga atoms is associated with a certain probability x_j. The total energy of each cluster is calculated by adopting a first-principles pseudopotential plane wave, within the framework of the density functional theory (DFT) and the local density approximation (LDA),[42,43] the so-called 'Vienna ab-initio simulation package' (VASP),[44,45] with the interaction between the valence electrons and the atomic cores treated by non-normconserving *ab initio* Vanderbilt pseudopotentials.[46] Within the GQCA the clusters with the energy ε_j used in the calculation of the internal energy should have a reasonable size. Clusters represented by four-atoms supercells, which is the smallest wurtzite unit cell, are too small. Such clusters do not yield information about the local correlation of the cations. The smallest clusters that consider local correlation are represented by the 16-atoms supercells. Therefore, 16-atoms supercells are used as the basic clusters to describe the fully relaxed alloys, as shown in Fig. 1. The structure of each cluster is optimized with respect to its lattice constants a, c and the internal parameter u, as well as, all atomic coordinates, via total energy minimization. A cluster with such a number of atoms is the smallest that allows a significant description of the alloy in this structure, taking into consideration local correlations. Each
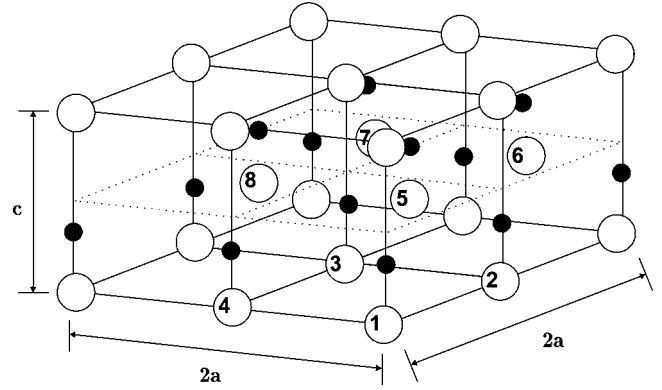

FIG. 1. Illustration of wurtzite structure and the positions of the ions in the cluster. The white balls represent the cations (indium or gallium) and the black balls represent the anions (nitrogen).

cluster cell is formed by the vectors $\vec{a}=2\vec{a}_1$, $\vec{b}=2\vec{a}_2$, and $\vec{c}=\vec{a}_3$, where $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$ are the base vectors of the primitive wurtzite cell.

If n_j is the number of indium atoms in the cluster j, there are $\binom{8}{n_j}$ different configurations for this cluster. So, the total number of configurations is $\Sigma_{n_j=0}^{8}\binom{8}{n_j}=256$. However, if we regard the energy degeneracy, this number is reduced and we get with 22 clusters in the end. These clusters are described in Table I.

For the wurtzite pseudobinary alloy $In_xGa_{1-x}N$ investigated here, we calculate the mixing free energy ΔF as a function of x and T at a fixed pressure, which allows us to access the temperature-composition (T-x) phase diagram and obtain the critical temperature for the miscibility. The mixing free energy ΔF is defined as the following:

$$\Delta F(x,T) = F(x,T) - xF_{InN}(x,T) - (1-x)F_{GaN}(x,T), \quad (1)$$

where F, F_{InN}, and F_{GaN} are, respectively, the Helmholtz free energies for the alloy, the pure InN compound, and the pure

TABLE I. All possible configurations of a 16 atoms wurtzite cell, where g_j is the degeneracy factor. It represents the number of ways of arranging the alloying cations in a cluster with energy ε_j. The corresponding numeration of indium atoms follows Fig. 1.

j	n_j	g_j	Indium atoms	j	n_j	g_j	Indium atoms
0	0	1		11	4	6	1,2,5,6
1	1	8	1	12	4	6	1,2,7,8
2	2	12	1,2	13	4	24	1,2,5,8
3	2	12	1,5	14	5	24	3,4,6,7,8
4	2	4	1,8	15	5	24	3,4,5,6,8
5	3	8	1,2,3	16	5	8	4,5,6,7,8
6	3	24	1,2,7	17	6	4	2,3,4,5,6,7
7	3	24	1,2,5	18	6	12	2,3,4,6,7,8
8	4	2	1,2,3,4	19	6	12	3,4,5,6,7,8
9	4	8	1,2,3,5	20	7	8	2,3,4,5,6,7,8
10	4	24	1,2,4,5	21	8	1	1,2,3,4,5,6,7,8

GaN compound containing the same number of N atoms. Then, ΔF can be written as

$$\Delta F(x,T) = \Delta U(x,T) - T\Delta S(x,T), \quad (2)$$

where ΔU is the mixing enthalpy and ΔS is the mixing entropy defined similarly to ΔF and given as in Refs. [33] and [40]. The calculations of the mixing free energies were carried out by combining the cluster expansion method within the framework of the GQCA and the self-consistent total-energy pseudopotential (VASP) calculations.

The configurationally averaged quantities describing a thermodynamic, a structural, or an electronic property P of the alloy are then given by a summation over the quantities being characteristic for each cluster P_j, and weighted by the fraction of clusters x_j,

$$P(x,T) = \sum_{j=0}^{J} x_j(x,T)P_j. \quad (3)$$

The definition above allows the introduction of fluctuations around the mean values by considering the mean-square (rms) deviations,

$$\Delta P(x,T) = \left[\sum_{j=0}^{J} x_j(x,T)P_j^2 - \left(\sum_{j=0}^{J} x_j(x,T)P_j \right)^2 \right]^{1/2}. \quad (4)$$

One of the resulting quantities, the average gap of the pseudobinary $In_xGa_{1-x}N$ alloy versus composition, at a fixed temperature T, can be described by the relation

$$E_g(x,T) = (1-x)E_g(GaN) + xE_g(InN) - bx(1-x), \quad (5)$$

with the bowing coefficient b, which characterizes the deviation from the linearity.

III. RESULTS AND DISCUSSION

In this section we present the results found for wurtzite $In_xGa_{1-x}N$ applying the method explained in the preceding section. For all structural and electronic properties we assume a growth temperature of 950 K, although the influence of the temperature variation, in the range of typical growth temperatures,[47,48] is negligible. We also emphasize, that in order to provide a better comparison between the obtained results for the W structure and the ZB ones, all the ZB results were previous results performed by the same research group, by using the same method.[33]

A. Structural properties

The GQCA allows us to build an expression for the mean value of any alloy structural property if the value of this property is known for all the clusters within the alloy. In Table II are listed the values for a and c lattice constants for every cluster considered in the calculation of the alloy.

We can write the mean values for these constants using Eq. (3),

TABLE II. Equilibrium lattice constants for the 22 clusters.

j	a_j(Å)	c_j(Å)	j	a_j(Å)	c_j(Å)
0	3.155	5.143	11	3.344	5.370
1	3.200	5.209	12	3.330	5.412
2	3.245	5.282	13	3.336	5.395
3	3.248	5.261	14	3.381	5.463
4	3.242	5.280	15	3.379	5.471
5	3.285	5.368	16	3.373	5.511
6	3.288	5.340	17	3.421	5.542
7	3.294	5.321	18	3.432	5.510
8	3.331	5.451	19	3.424	5.547
9	3.338	5.402	20	3.470	5.608
10	3.333	5.416	21	3.514	5.684

$$a(x,T) = \sum_{j=0}^{21} x_j(x,T)a_j \quad \text{and} \quad c(x,T) = \sum_{j=0}^{21} x_j(x,T)c_j, \quad (6)$$

with a_j and c_j the lattice constants of each cluster listed in Table II

In Fig. 2 we show how these values vary with the concentration. We confront these results with linear behavior predicted by Vegard's law[49] for a fixed temperature,

$$a(x,T) = xa_{InN} + (1-x)a_{GaN}$$

$$c(x,T) = xc_{InN} + (1-x)c_{GaN}. \quad (7)$$

We can observe a linear behavior for both lattice constants a and c, being the first in very good agreement with the Vegard's law while the latter presents a slight deviation from the linearity. By calculating the shift
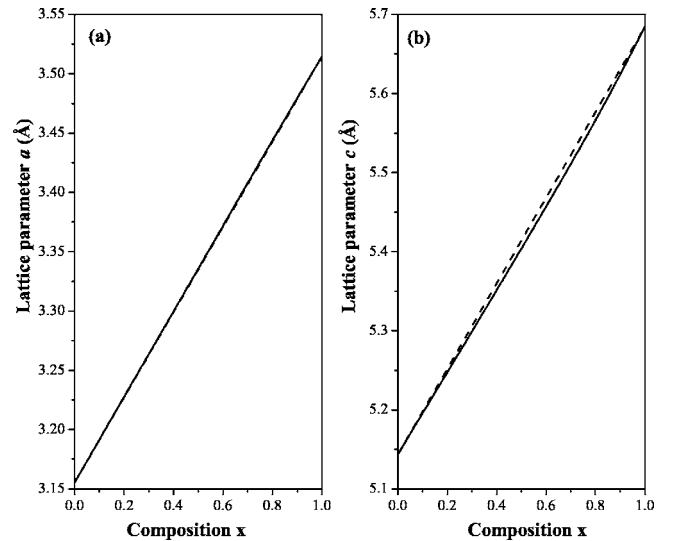

FIG. 2. Mean value of lattice constants a and c (solid line) vs In composition for relaxed $In_xGa_{1-x}N$ compared to values foreseen from Vegard law (dashed line).
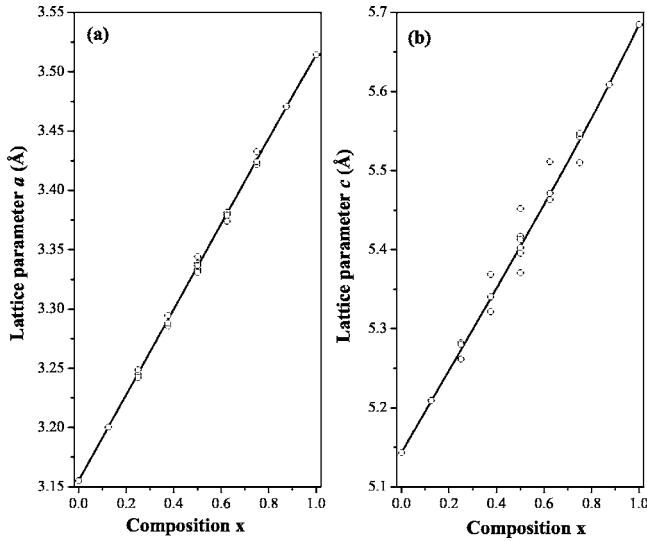
FIG. 3. Mean value of lattice constants a and c (solid line) in relaxed $In_xGa_{1-x}N$ alloys, and the lattice constants a_j and c_j of each calculated cluster.

$$\sigma(x) = \frac{c(x) - c_V(x)}{c_V(x)}, \qquad (8)$$

with $c_V(x)$ being the expected valued from Vegard's law, we found a maximum value of 0.2% for $x=0.67$. Mattila *et al.* found for the zinc-blende structure value for $\sigma(x)$ of -0.39% for $x=0.50$ and -0.30% for $x=0.25$ or 0.75.[29] Ferhat *et al.* also found a slight deviation from Vegard's law for the ZB structure, which was attributed to the reason that within large supercells the local InN regions tend to have large lattice constants.[50] In our previous calculations for the ZB structure, which take into account the alloy statistics, we found that the Vegard's law is fulfilled (considering 8 or 16 atoms per cell).[33,36] Although, another recent work,[51] also performed for the *W*-InGaN, found a larger deviation from the linearity. In order to quantify this deviation the authors calculated the corresponding analogous bowing parameter[52] for the lattice constants a and c, δ_a and δ_c, respectively, and found $\delta_a = 0.047$ Å and $\delta_c = -0.117$ Å. According to our results the values for the lattice parameters bowing are $\delta_a = -0.004$ Å and $\delta_c = 0.042$ Å. Qualitatively, both results reveal a larger deviation from Vegard's law for the c constants, but quantitatively, the results present a discrepancy. We attribute this discrepancy to the fact that in Ref. 51 the authors used a specific configuration and did not take into account any alloy statistics nor configuration average, and we assume the same reason for the discrepancy with the other calculations,[29,50,51] which also assume for obtaining the alloy properties only one or a few alloy configurations. In order to verify this assumption we plotted the results obtained for each cluster representing the different configurations. The results are shown in Fig. 3. From this figure we can observe that by choosing different configurations without taking into account the statistics we can find different values for the deviation from the linearity, but when the statistics (considering all possible configurations) is taken into account the result be-
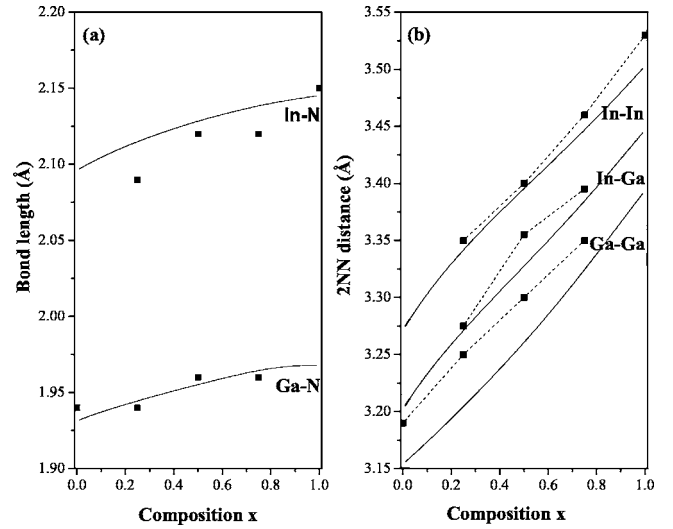

FIG. 4. Averaged bond lengths (a) and second-nearest-neighbor distances (b) (solid line) in relaxed $In_xGa_{1-x}N$ alloys. The filled squares describe measured values obtained by EXAFS (Ref. 53).

comes very similar to the Vegard's law, which in fact explain the discrepancy, when present, between our results and the others,[29,50,51] and leads to the conclusion that the consideration of alloy statistics is crucial to obtain more reliable results.

Now we focus our attention on the bond lengths d_{InN} and d_{GaN}, as well as, second-nearest-neighbors distances (2NN) d_{InIn}, d_{GaGa}, and d_{InGa}. In order to analyze these properties, we reformulate Eq. (3),[33]

$$d_{X\text{-}Y} = \frac{\sum_{j=0}^{21} x_j n_{X\text{-}Y}^j d_{X\text{-}Y}^j}{\sum_{j=0}^{21} x_j n_{X\text{-}Y}^j}, \qquad (9)$$

where $d_{X\text{-}Y}^j$ and $n_{X\text{-}Y}^j$ are, respectively, the length and the relative number of $X\text{-}Y$ bonds within the cluster j. The calculated and experimental values are illustrated graphically in Fig. 4 as a function of the alloy composition. The experimental data points were measured by the extended x-ray absorption fine structure (EXAFS) technique for samples grown using molecular beam epitaxy (MBE).[53] We can observe the same behavior as the previous results obtained for the cubic structure, where the bond lengths try to have the same values as in the corresponding binary compounds and be composition independent, only the weighted concentration average bond length reaches the limit given by Vegard's law, and for the 2NN, three distinct values are observed. The magnitude of $d_{X\text{-}Y}$ follows the covalent radii of the contributing atoms.[33,36,50] We can also note an improvement considering the quantitative agreement between the calculated and experimental results in comparison with the ZB previous results.[33] We can also observe a good agreement between our results and previous calculations.[28,29,31]
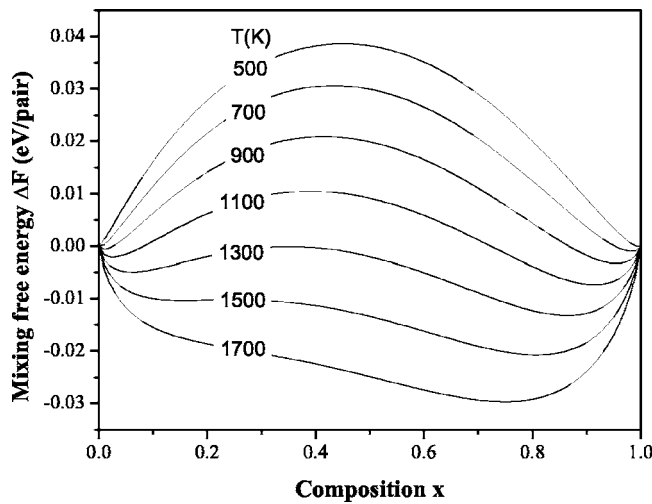
FIG. 5. Mixing free energy $\Delta F(x,T)$ of In$_x$Ga$_{1-x}$N wurtzite versus composition.

B. Phase stability

In order to study the phase stability of the W-In$_x$Ga$_{1-x}$N random alloys, we calculate the Helmholtz free energy of the alloy and the T-x phase diagram. In Fig. 5 we show the variation of the free energy as a function of the concentration for some values of the temperature. Figure 6 depicts the phase diagram obtained results and the previous one for the ZB structure.[33] More in detail it shows the spinodal and binodal curves calculated within the GQCA and the *ab initio* total energy method. The spinodal curve in the phase diagram marks the equilibrium solubility limit, i.e., the miscibility gap. Within the miscibility gap a single given solid solution is unstable against decomposition into alloys with
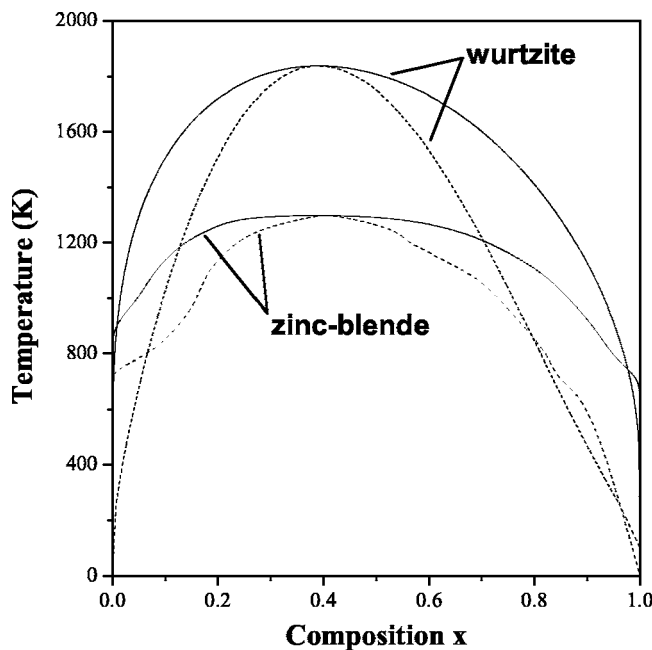

FIG. 6. Phase diagram of In$_x$Ga$_{1-x}$N alloys at hexagonal and cubic structures. The solid lines represent the binodal curves and dashed lines are the spinodal curves.

different compositions. Above a certain critical temperature the alloy is stable for any composition. From our results, we can observe that the critical temperature is considerably higher for the W structure ($T_{crit}=1839$ K) in comparison to the ZB one ($T_{crit}=1295$ K). Although another interesting fact can also be observed: in the range of growth temperatures (800 K to 1000 K), we observe a phase separation for more or less the same wide range of composition. Considering, e.g., $T=900$ K, a large decomposition tendency is seen for In content between 8% to 79% for the W structure and between 12% to 78% for the ZB one, which means that for a certain range of temperatures the In-rich clusters will tend to have the same composition in both structures. This result is in good agreement with experimental findings that show a tendency to phase separation.[54–58] There are several theoretical works in the literature which analyze the thermodynamic stability in the InGaN alloy, and all of them use the strictly regular solution model, with only one[12,21,25,28,59] or a few[50] alloy configurations. They found a range for the critical temperature which varies from ~1200 to 2500 K. The phase diagram shown in Fig. 6 is more asymmetric, and we obtain a larger range of miscibility for higher In molar fractions x.

C. Electronic properties: Energy gap and bowing parameter

InGaN represents the active media in the group-III nitride-based devices, as the blue lasers diodes (LDs) and light-emitting diodes (LEDs). And as a fundamental property to be studied there is the fundamental energy gap. The fundamental gap of the W-InGaN is found at Γ point of the Brillouin zone. For GaN and InN we found $E_g=2.208$ eV and $E_g=-0.021$ eV, respectively. By using the GQCA method, considering the alloy statistics, we evaluate the mean value of gap. Fortunately, the quasiparticle corrections for the energy gap vary almost linearly with the composition, as shown previously for the ternary nitride alloys[60] and we can obtain a reliable value for the bowing parameter. Figure 7 shows the alloy band gap as a function of In composition, where we apply a linear shift in the band gap of the alloy in order to have the values for the gap energy of the binary compounds GaN and InN comparable with the experimental ones ($E_g^{GaN}=3.42$ eV and $E_g^{InN}=0.77$ eV).[34,36,61] The composition dependence of the band gap can be determined by Eq. (5). From the results shown in Fig. 7 we can clearly observe a downward bowing of the energy gap with a bowing parameter $b=1.44$ eV.

Once the wurtzite and zinc-blende Γ gaps for the binaries compounds are very similar, with the wurtzite gap being slightly larger,[23] there is a common expectation that the bowing parameter should also be very similar for both alloy structures. By comparing this result to the previously obtained for the ZB structure, we observe that the present value for b is slightly larger than that obtained in the ZB calculations (1.37 eV).[36]

The reliability of early determinations of the energy gap bowing parameter for the InGaN must now be questioned in light of the considerable overestimate of the InN gap.[6] Recent works have produced considerable progress in funda-
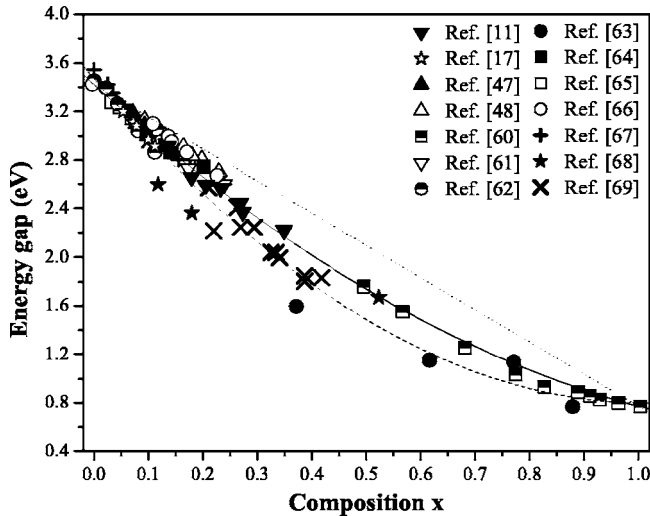
FIG. 7. Calculated energy gap E_g (solid line) compared to the experimental data (different symbols). The dotted line represents the E_g according to Vegard's rule and the dashed line is the fit of McCluskey (Ref. 17): $E_g = 3.47(1-x) + 0.8x - 2.6x(1-x)$.

mental understanding of the InGaN energy gap.[6] Although, it is worth noting that there are still discussions and contradictions about the bowing value in the literature. Recently, Wu *et al.* by optical absorption and photoluminescence measurements showed that band gap versus composition is well described by a bowing parameter of ∼1.4 eV, with which our results present a very good agreement.[9] However, McCluskey *et al.*, by also carrying out optical absorption spectroscopy measurements on pseudomorphic InGaN layers grown on GaN, inferred the band gap of relaxed InGaN by subtracting the contribution due to biaxial strain.[17] The bowing parameter obtained by these authors is 2.6 eV for a InN gap of 0.8 eV, which shows a very large discrepancy with the results of Wu *et al.*[15,61]

In order to compare our results with the experimental ones, we plot in Fig. 7 several other experimental results,[11,17,47,48,61–70] including the more recent ones of McCluskey *et al.*[17] and Wu *et al.*[61] It is worth pointing out that the InGaN alloys may present phase separation, which may change the emission mechanism, and that our results for the energy gap are for a random alloy, diregarding phase separation process. From Fig. 7 we can observe that our result is in very good agreement with the major experimental data, for a large range of In compositions, including the experimental data of McCluskey *et al.* (with exception of one data point at $x = 0.112$, which presents an energy gap value slightly different $E_g = 2.91$ eV from our obtained value $E_g = 2.98$ eV). In Fig. 7 the dashed curve represents the fit of McCluskey. It is very clear that it represents the best fit with its own results, but not with the major experimental findings, if we exclude O'Donnell.[70] O'Donnell *et al.* in Ref. 70, speculated on the possibility of nanostructure, or a common localization mechanism responsible for InGaN lumines-

cence. We believe that to obtain a good estimate of the bowing parameter, data for a large range of In composition are necessary, and that the determination of b by using a small set of experimental data for a small range of In composition can lead to a misunderstanding of the bowing value. We attribute the same reason for the discrepancy with the theoretical values obtained by McCluskey *et al.* (performed only for $x = 0.0625$ and 0.125). Attended to this fact, we performed careful calculations with all configurations for all ranges of In composition, by considering the alloy statistics. Therefore we believe that our value is reliable and gives support to the recent claim that InGaN exhibits a small band gap bowing.

IV. SUMMARY

In summary, we have presented studies of thermodynamic, structural, and electronic properties of unstrained wurtzite $In_xGa_{1-x}N$ alloys by combining first-principles total energy calculations and the generalized quasichemical approach. We emphasized the importance of taking into account the alloy statistics to obtain reliable results. We calculated the lattice constants, bond lengths, second-nearest-neighbors distances in the alloy. Concerning the electronic properties, we evaluated the energy gap and found that our result presents very good agreement with the experimental findings for a broad composition range, supporting for the smaller band gap bowing findings of ∼1.4 eV. We tried to explain the seemingly contradicting experimental findings, showing that for a more reliable result one needs a considerably broadened composition range over which the bowing can be determined.

It is worth pointing out that the results presented here for InGaN have been obtained for bulk materials, and surface effects were not taken into consideration. Moreover, the model theory adopted here is able to interpret recent experimental data on these nitride alloy layers in both ZB and *W* structures. Finally, by comparing the results obtained for both structures, in order to avoid differences coming from the size of the supercell we considered the same number of 16 atoms per cell. We found that structural and electronic properties do not show significant difference between the results for ZB and *W* structure. Therefore, our results give support to the ZB predictions. Considering the phase stability, we found that the critical temperature is reasonably higher for the *W* structure than for the ZB one. Although, for the typical range of growth temperatures, we could observe a similar range of composition for which the alloy tends to phase separate.

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